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DISPOSAL OF PYROTECHNIC ILLUMINATING AND SIGNALLING AMMUNITION

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Abstract

Pyrotechnic illuminating and signalling ammunition is subject of a natural aging because of the chemical behavior of the used pyrotechnic compositions and sub-assemblies. For this reason the durability is limited and the use for its purpose is not longer possible because of the safety aspects.

From the substance properties of the pyrotechnic compositions in illuminating and signalling ammunition starting points are given which lead the disposal to an environmental friendly, extensive recycling of materials. Started from a short description of the design of illuminating and signalling ammunition and the disposal task the practicise diposal processes are demonstrated in a general view.

The exemplarey disposal of pyrotechnic ammunitions in the plant of a German enterprise demonstrates the manifold problems and their solution at the completion of a contract for disposal.

By means of real measurement results for the emission situation the requirements of the environment protection, the approval process according to the German law and the experiences from the operation of the plant are explained.

A special attention is drawn to the engineering solution as well as the measuring technique in context with the emission control.

Finally a view is given to the actual problems of the disposal of illuminating and signalling ammunition.

1. Objectives of Pyrotechnics Disposal – Illuminating and Signal Ammunition

Pyrotechnics are generally described as products with which a flash, smoke, noise or other effects are produced, either for pleasure, as in the case for firework, or for military or technical purposes. These effects are produced via the chemical reaction of solid matter mixtures, that is, the pyrotechnic charges.

The tradition of fireworks reaches back over two thousand years to the cultures of ancient China and Greece, and both these countries also used pyrotechnical charges for military purposes.

A pyrotechnical charge is the determining constituent of a pyrotechnical product, and is composed of solid combustible matter and an oxidiser, together with binding agents and combustion moderators, which all help to produce the effects desired via self-sustaining combustion.

Pyrotechnic mixtures represent explosive charges, which means that the appropriate precautinary measures must be observed, not only during handling in general, but also in respect of cleanless during manufacture and disposal. Pyrotechnical charges are manufactured in accordance with exact formulations, and the chemical composition is analysed during the manufacture and processing stages.

In so far as pyrotechnical products are not used, in other words fired in accordance with regulations, they are subject to the influences of temperature and humiditiy, and therefore a natural ageing process. There is therefore a requirement for disposal of products which have been stored in excess of their shelf life, or otherwise become unserviceable.

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The alterations in the substance structure and, under certain circumtances, the chemical composition of pyrotechnic charges, which go hand in hand with the ageing process, can lead only to desensitising, but also to sensitisation of the products. Such processes must be taken into account when handling pyrotechnic charges during disposal.

Pyrotechnic products, however, are not classified as waste in the generally accepted sense, but as products with defined properties, in other words, products defined with regard to their chemical and explosive properties. Any disposal of pyrotechnical products in accordance with the regulations applying to hazardous waste must therefore be ruled out, due to classification of these products as explosive charges.

Pyrotechnic production waste in the form of faulty batched, scrapped material, dust from sweepings or secondary materials which have been treated with explosive charges, such as paper of plastic, pose a separate disposal problem. On the one hand, factory safety must be ensured during the manufacturing process by a strict system of residual material detection, separation of individual substances and safe handling of materials. On the other hand, this system must ensure the strict definition of the materials to be disposed of, and enable the preliminary treatment of these materials, for example in the form of a desensitising process, as and when required. The discussion will, however, not be entered to in this paper.

The subject in this paper concerns the problems arising out of the disposal of pyrotechnics produced for military purposes.

A number of recycling and disposal concepts for pyrotechnical products have been developed by various companies over the last few years, and introduced in connection with the disposal of the superfluous inventory of the former East German Army. These concepts ensure not only the most extensive recycling of the constituents, but also fulfilment of the requirements with regard to the handling of explosive charges and environmental protection.

In the course of the performance of this disposal task an a large technical scale, and its extension to the inventory of pyrotechnic ammunition of the Bundeswehr and the armed forces of other states stored in excess of their shelf life, many facts have been established and valuable experience gained.

It has become apparent that the task of pyrotechnics disposal, which includes the following classes of explosive ordnance, must take different methods of disposal into account when concepts demanding the most extensive utilisation of materials are introduced:

- Pyrotechnic illumination and signal ammunition and agents
- Simulation agents, in particular battle noise simulation charges
- HC smoke agents
- RP and WP smoke agents
- Other incendiary agents
- Pyrotechnic agents containing HE
- Propellant powder
- Igniters, in particular those containing Hg

Starting form the exact supervision, determination and classification of the explosive ordnance received for disposal, a most extensive breakdown of the products with separation of invidual constituents is required. Figure 1 refers. The next stage involves the recirculation of residual material in the cycle of materials.

Due to the presence of explosive charges, pyrotechnic constituents, which are generally non-recyclable, must be subjected directly, or following appropriate preliminary treatment, to disposal by combustion in special facilities. Other disposal procedures have, however, been developed with regard to special cases and are applied to the disposal process.

With regard to the disposal of the pyrotechnic constituents of the pyrotechnic illumination and signal ammunition discussed within the framework of this presentation, only combustion facilities in various states of completion can, as a rule, be taken into consideration.

A comparison of the requirement or separation with the feasibility of subsequent material sales underlines the fact that no other solution is possible with regard to the disposal of pyrotechnic charges or pellets. The one exception is black powder in bulk form, which can be used for fireworks.

The groups of substances to be disposed of, together with the disposal steps required in connection with a simple detonation charge, are provided in diagram form at Figure 2. The types of explosive substances obtained during disposal are provided at Figure 3.

2. Disposal Facility Concept

The recycling of pyrotechnic constituents, in other words of pyrotechnic charges, is, as a rule, not possible, either for safety reasons or cost factors. Pyrotechnic constituents are therefore either converted under closely supervised conditions in accordance with handling regulations, or subjected to combustion in a combustion facility. All dust particles and combustion gases generated during these processes are drawn off and input to a waste gas purification facility.

During the process, the natural properties of pyrotechnical charges, that is the capability of self-sustaining combustion due to the „built-in“ oxidiser, together with alkaline effects of the alkaline and alkaline-earth metal solid oxides and carbonates formed, are used to support combustion and waste gas purification.

The concept of a combustion disposal facility is determined not only by the predicted mass throughout of the components, but also by the components to be disposed of. The concept of a comprehensive combustion facility is included at Figure 4. Processes can be eliminated according to the individual field of application.

The combustion facility conceived solely for the disposal of pyrotechnics in the Pyrotechnik Silberhütte Company includes the following component groups. Figure 5 and 6 refer.

- *Combustion Facility*

  Conversion of pyrotechnic charges at combustion temperatures between 2,000 and 3,000 degrees centigrade.

- *Air Condenser as Quench*

  Reduction of waste gas temperature and simultanious preliminary separation and combustion protection.

- *Jet Impulse Bag Filter*

  Alkaline dry purification and dust separation

- *Emission Monitoring Test Section*

  Continuous determination of emission relevant values

- *Induced Draught Fan with Waste Air Chimney*

All dust particles generated are filled via discharge facilities into sheet steel barrels, which are currently stored in an underground waste dump. Although further treatment of filter dust particles is planned, realisation of the process is at present not possible due to the current costing structure in force with regard to recoverable substances.

The input of substances for combustion ist performed via an automatic input facility for safety reasons.

A facility for the recycling of pyrotechnic products such as one described is subject to the Federal Immission Control Act, as are all pyrotechnic facilities.

Although open combustion is specified in current regulatios for explosives factories as a requirement for operational authorisation, new ground is broken by a combustion facility with integrated waste gas purification. Initial operating experience has shown not only that a reduction in emissions has been achieved, but also that pecularities in the operation of the facility demand special operating methods which deviate distinctly from those currently in use in hazardous waste incineration facilities.

Since approximately 80 – 90 per cent of pyrotechnic substances input to combustion is converted to alkaline dust particles, the separation of these particles is the main problem with regard to the purification of waste gas.

The disposal procedure described in this paper is based on the principle of conformity between the reaction conditions in the facility and its operation in accordance with regulations, together with the avoidance as far as possible of any transfer to other media during the waste gas purification stage. It is for this reason that open combustion and dry waste gas purification, in other words, a procedure dispensing with the use of water, was chosen.

Fulfilment of the emission value requirements of the Federal Immission Control Act, Regulation 17, was demonstrated within the framework of the authorisation procedure.

3. Procedural Principles and Results of Emission Monitoring

Typical compositions of pyrotechnics used for military purposes are as follows:

Mg	48 %	Composition „yellow“
$NaNo_3$	43 %	
Mg Stearate $[Mg(C_{18}H_{35}O_2)]$	2 %	
Varnish $[C_{16}H_{26}O_2]$	8 %	

Mg	29 %	Composition „red“
KNo_3	14 %	
$SrNo_3$	40 %	
PVC $[(C_2H_3Cl)_n]$	10 %	
Varnish	7 %	

Mg	40 %	Composition „green“
$Ba(No_3)_2$	40 %	
PVC	15 %	
Varnish	5 %	

There are also the following combustible compositions in form of black powder:

KNo_3	75 %
S	10 %
C	15 %

Finally, there are various intermediate charges, for example:

Mg	16 %
KNo$_3$	75 %
Novolak	9 %
[CH(C_6H_4OH)$_2$]	

Taking the „yellow" main charges and a requirement for total conversion as an example approximately 900 g/kg solid combustion products are generated, for example MgO, K_2O, Na_2O, together with approximately 315g/kg gaseous constituents. Estimated as a percentage of the original pyrotechnic charge, these figures amount to approximately 90% in form of solid matter, and 10% in the form of gaseous constituents.

The existence of complicated conditions can be inferred from the actually recorded values of the gas analysis and the ash and filter residue, however.

An overview of emission ratios recorded to date in respect of pyrotechnics with the composition Me-MeNitrate is included at Table 1. These ratios based solely on the gas measurements recorded in the combustion facility.

It will be clear that the test data are effected to a great extent by the operating conditions of the facility, in other words by the temperature of the facility with regard to the generation of thermal NO_x, as well as by the oxygen available with regard to the conversion of CO.

With regard to the open combustion of pyrotechnic ammunition in accordance with regulations, this means that the conditions conducive to the generation of NO_x and CO are much more favourable, that is to say, less NO_x and CO are generated than in an established combustion facility. The analyses of filter dust and slag discharge provided the values which were to be expected.

The alkaline and alkline earth elements used are recovered in the form of oxides, carbonates, nitrites, nitrates and, in certain cases, chlorides. Carbide can also be found under certain conditions.

Only traces of heavy metals were recorded. This assumes, of course, that such metals are not present at the start of combustion cycle, for example CuO or $SbSO_3$.

An eluate analysis of filter discharge and ash residue of the above compositions is included in Table 2. A (theoretical) computer projection of filter dust composition based on analyses results is included at Table 3.

The precense of Strontium is not critical. No Sr^{90} was recorded !!!

Soluble barium compounds in the form of semi-toxic substances are transformed in practice into sulfates or carbonates an then immobile.

This problem, together with the high solubility, must be taken into account when filter and ash residue is dumped.

Table 3: Results of the Filter Dust Analysis

Coarse Dust:		
MgO	- 46.8	Percentage Weight
$(Na/K)_2O$	- 14	„
SiO_2	- 9	„
$MgCO_3$	- 9.3	„
H_2O	- 8.5	„
Fe_2O_3	- 3.7	„
$CaCO_3$	- 2.3	„
$SrCO_3$	- 1.5	„
Al_2O_3	- 1.4	„
$SrSO_4$	- 1.4	„
$BaSO_4$	- 0.8	„
$(Na/K)Cl$	- 0.6	„
$ZnCO_3$	- 0.4	„
Fine Dust:		
MgO	- 67	Percentage Weight
$(Na/K)_2O$	- 14.3	„
$MgCO_3$	- 7.0	„
$BaCO_3$	- 4.4	„
$SrCO_3$	- 3.1	„
$(Na/K)Cl$	- 1.6	„
H_2O	- 1.6	„
$BaSO_4$	- 1.0	„
$(Na/K)Cl$	- 0.6	„
$ZnCO_3$	- 0.4	„
Dioxin / Furan		
Toxicity Equivalency iaw NATO	- 0.2 ng/kg	

Selected facility operating data is presented in the following figures. A history of daily averages for a typical month is presented at Figure 7. A typical history of half-hourly mean value is presented at Figure 8.

The combustion behaviour of bulk pyrotechnical charges, for example detonation charges, must be analysed prior to their disposal. Charges of sensitivity grouping 4 or 5 can be directly input to a combustion facility in small amounts, for example smoke charges containing HCH. Charges with a higher speed of reaction must be desensi-tised prior to combustion. Desentisitation can be effected either by the addtion of en-doergic agents, or by converting the oxygen constiuent into supercritical form. The participation of desentisiting agents in combustion reactions in connection with the generation of waste products must be taken into account. This applies also to the effect of inert agents.

The occurence of stable reactions must be ensured in every case. In addition, the technical devises used in the input and combustion processes must be capable of preventing a reaction at the input position and therefore a hazard to personnel and the facility itself.

4. Conclusions

The following conclusions can be stated:

1. Procedures have been developed for the recycling of pyrotechnic products, including combustion of the pyrotechnic charges, and are currently being applied.

2. Additional investigations have demonstrated that the procedures are also suit- able for the combustion of bulk pyrotechnic charges.

3. Immission control requirements in accordance with Regulation 17 of the Fede-ral Immission Control Act can be fulfilled.

4. Constituent reprocessing procedures can be used with regard to special forms and configurations of pyrotechnic products.

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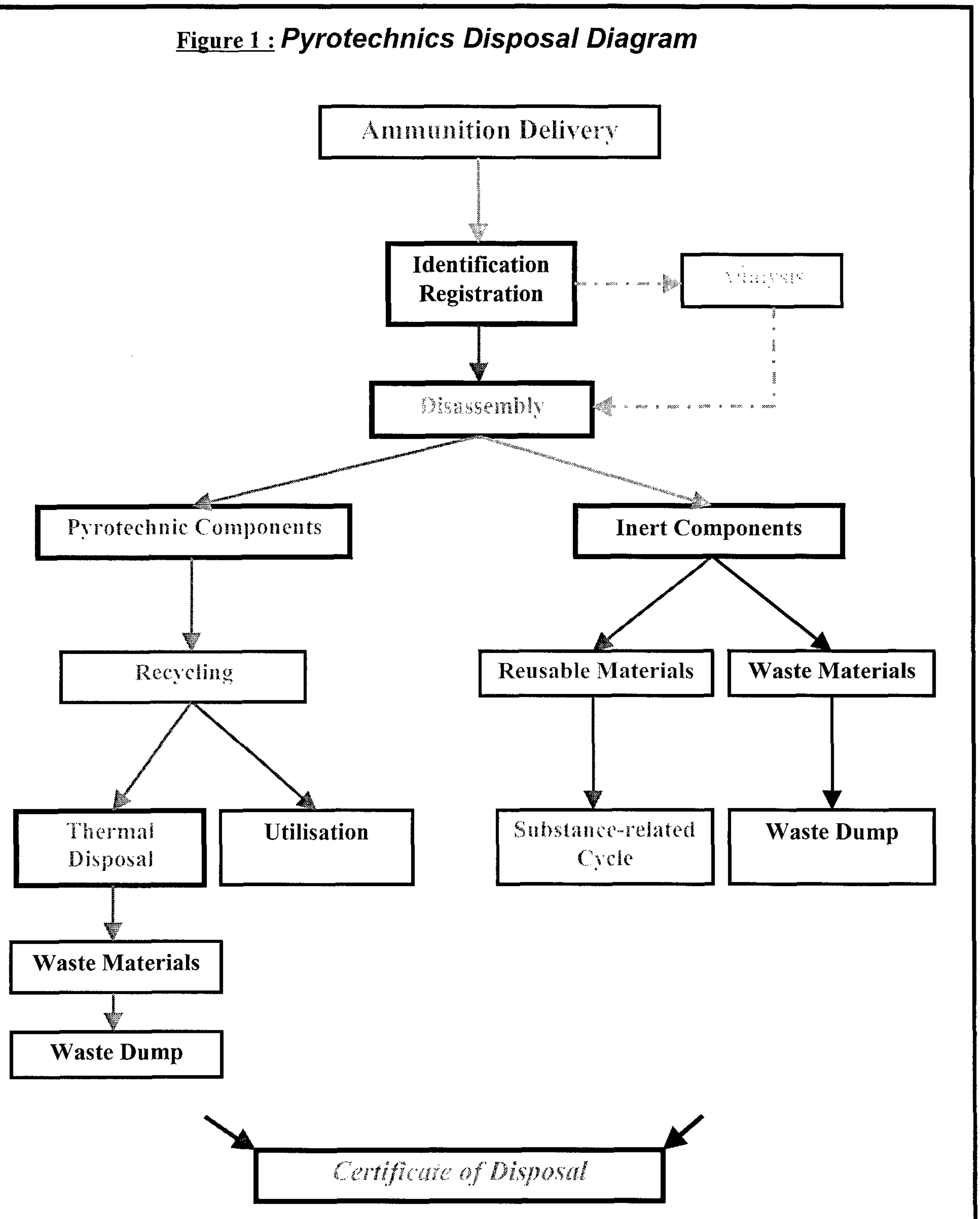

Table 1: Gas Composition Based on Gas Measurements Alone

Composition	NOx	CO	V	m	STB*)	SO_2	HCl	Total C	TE
	mg/m³	mg/m³	m³/h	kg/h	mg/m³	mg/m³	mg/m³	mg/m³	ng/m³
„Yellow“	258±50	7.5±0.8	6939±1081	73	0.19±0.04	1.57±0.18	1.20±0.8	2.35±0.93	0.002
„Red“	47±15	24±12	7685±623	74	0.17±0.01	1.63±0.06	0.39±0.02	0.08	-
„Green“	47±11	13±6	7251±400	89	0.17±0.02	1.54±0.11	0.45±0.05	2.46±1.74	0.004
„Yellow2“**)	178.4	29.4	5458	94	0.0	2.58	n.g.	n.g.	n.g.

*) - Solid Particle Ratio 92.8 %

**)- Mean Values recorded on 22 March 93

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Table 2 : Results of Eluate analysis of Solid Combustion Products

Composition		yellow		green		red
Dust	**Dimension**	**coarse**	**fine**	**coarse**	**fine**	**fine**
pH-Value		11.62	12.73	11.52	12.92	12.98
Conductivity	mS/cm	18.6	40.1	14.9	47.8	49.0
Lead	mg/l	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01
Copper	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Mercury	mg/l	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Cadmium	mg/l	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Zinc	mg/l	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Chromium	mg/l	< 0.01	< 0.05	< 0.01	< 0.01	< 0.02
Chromium (IV)	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Nickel	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Vanadium	mg/l	< 0.01	< 0.01	0.17	0.21	< 0.01
Antimony	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cobalt	mg/l	0.01	0.02	< 0.01	0.09	0.02
Arsenic	mg/l	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Thallium	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Tin	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Selenium	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Barium	mg/l	14	31	8050	9500	8.2
Ammonium	mg/l	10.6	< 0.5	2.44	0.64	< 0.5
Chloride	mg/l	37	130	4700	6900	7400
Nitrate	mg/l	0.85	8.5	< 0.1	1.6	5.4
Nitrite	mg/l	< 0.2	9.8	< 0.2	0.25	< 0.2
Sulphate	mg/l	131	282	< 0.5	< 0.5	630
Fluoride	mg/l	0.1	< 0.1	< 0.1	< 0.1	0.26
Cyanide (perturbed)	mg/l	< 0.03	< 0.03	2.6	0.03	< 0.03
AOX (perturbed)	mg/l	< 0.01	< 0.01	< 0.01	0.19	0.22
TOC	mg/l	< 5	< 5	< 5	< 5	< 5
PAH iaw German Drinking Water regulations	mg/l	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001

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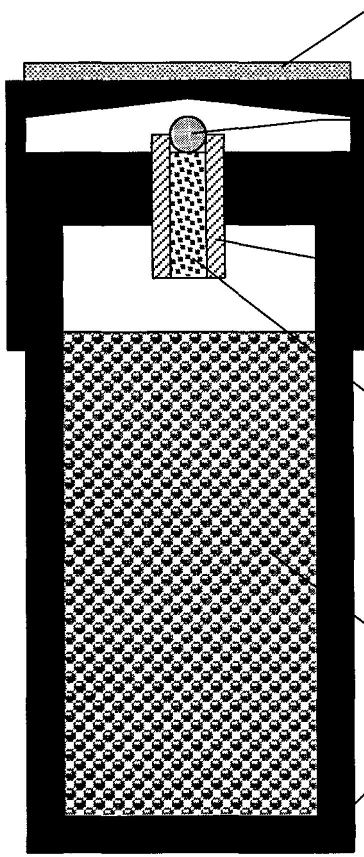

Friction Surface	- Paper, RP-Mix
Cap	- Cardboard
Igniter	- Pyrotechnic Charge ($KClO_3/Ba(NO_3)_2$/S/Binder)
Plug	- PVC-Moulding
Delay tube	- Brass
Delay tube charge	- Pyrotechnic Charge (Black Powder)
Detonating charge	- Pyrotechnic Charge (Al / $KClO_4$)
Case	- Cardboard, impregnated with Phenolic Laquer

<u>Figure 2 :</u>

Thunderflash

Assembly

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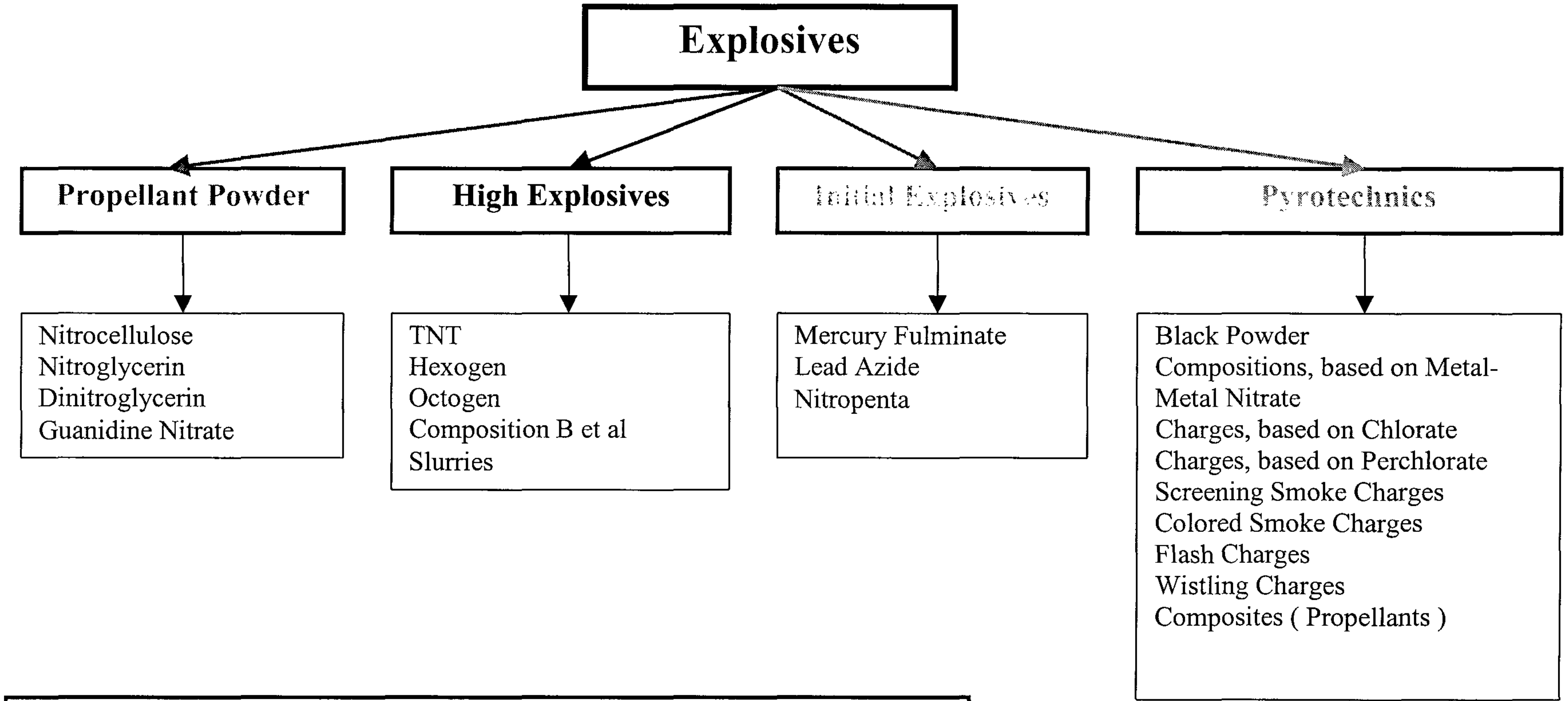

Figure 3 :

Explosives Recovered during Explosive Ordnance Disposal

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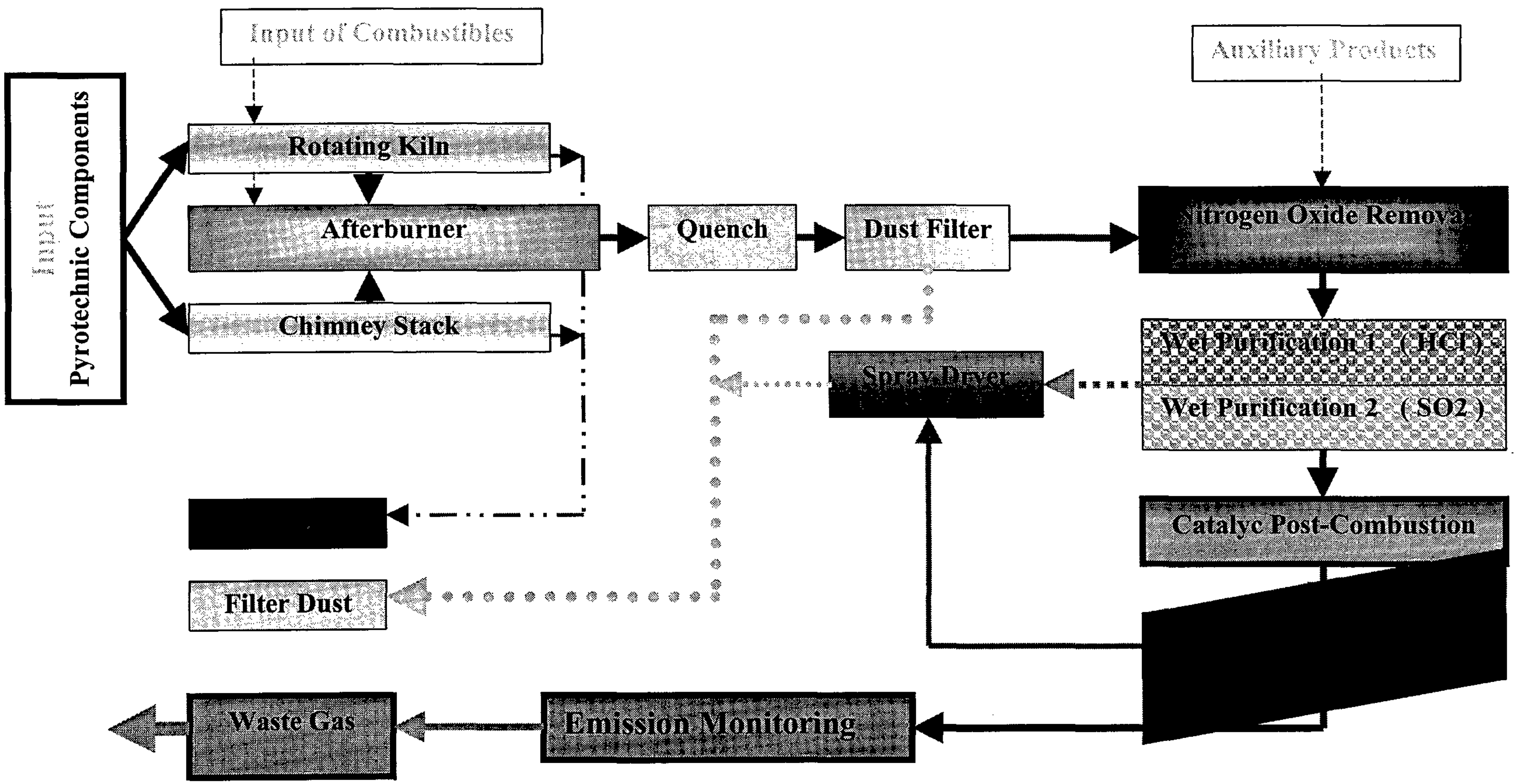
Figure 4 : Thermal Disposal Facility Diagram



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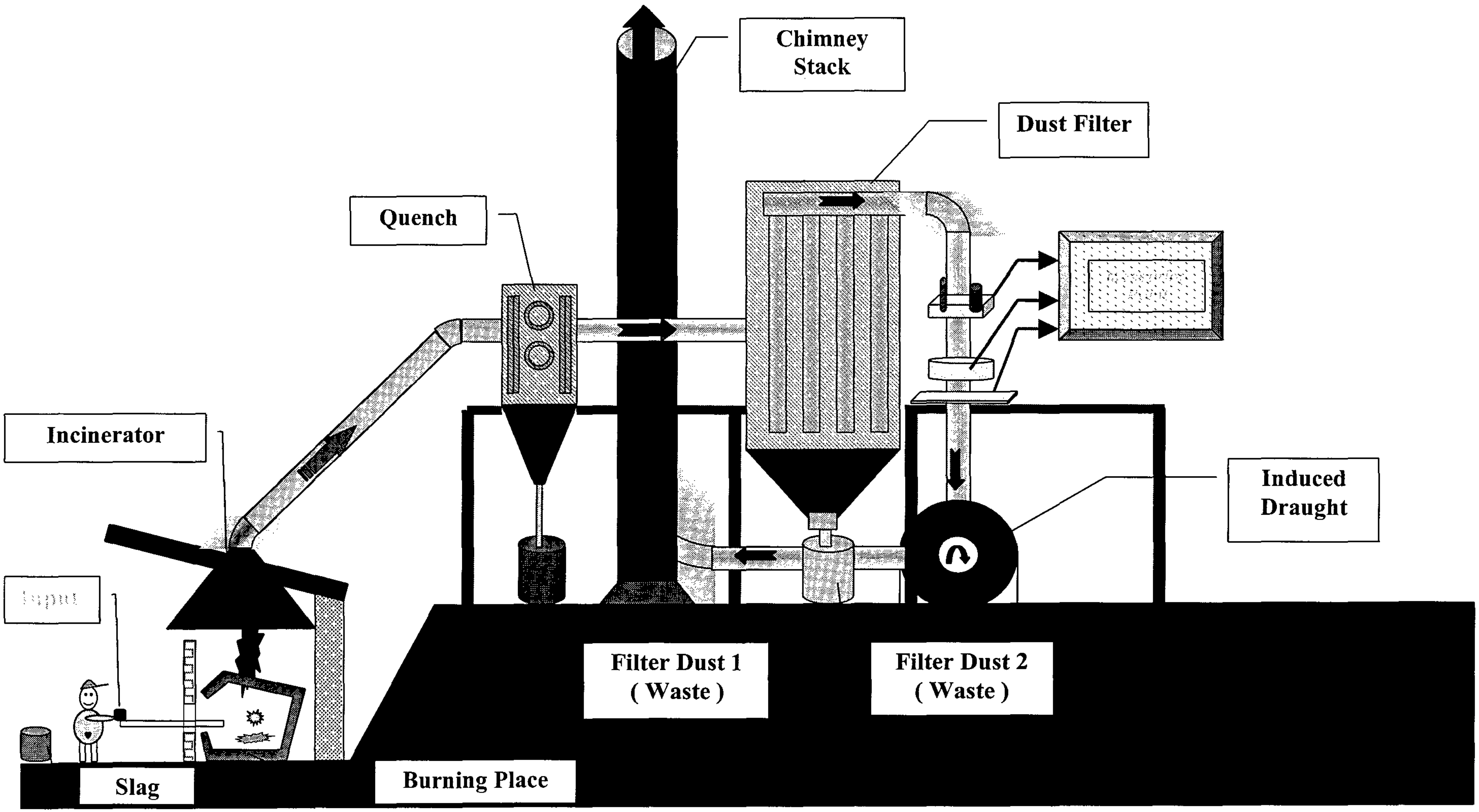
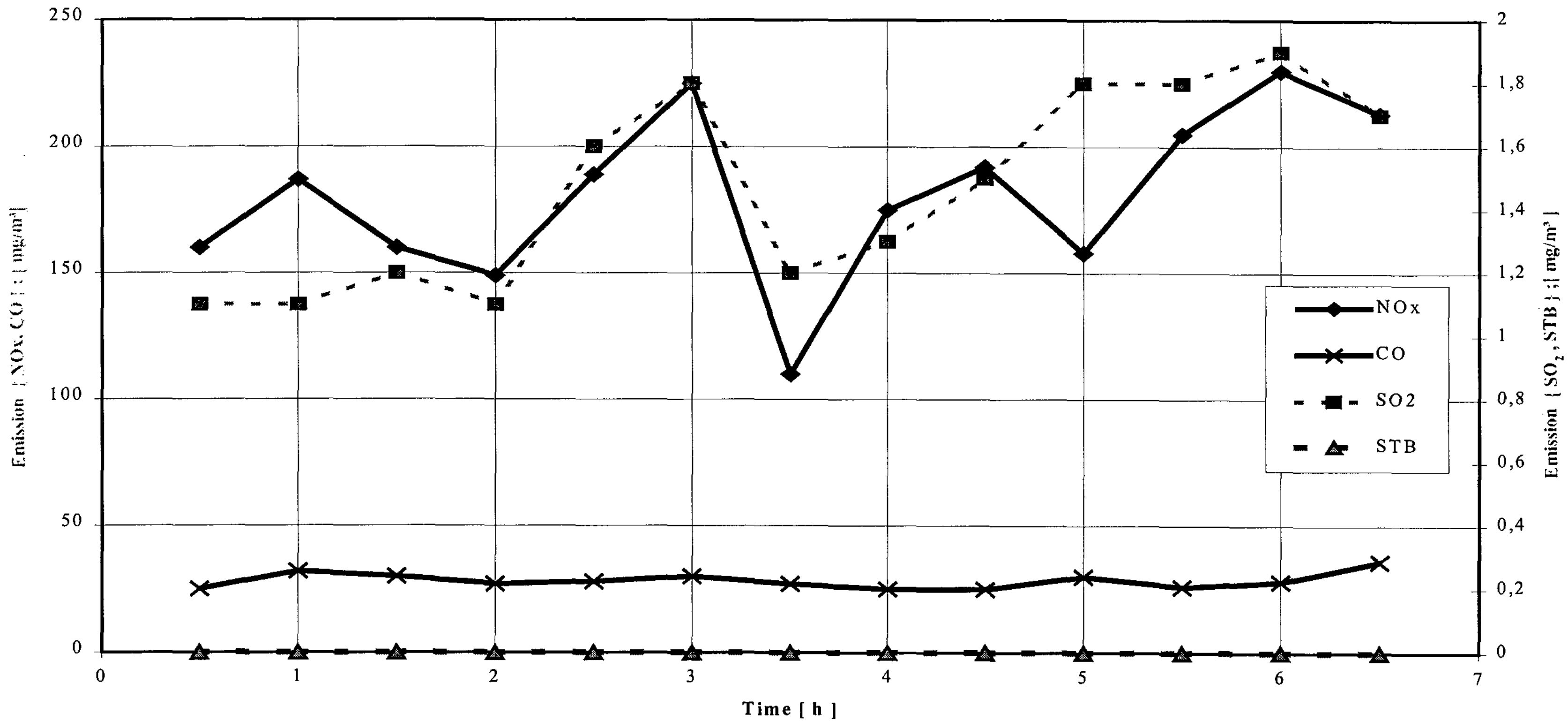


Figure 5 : *Thermal Utilisation Diagram - Silberhütte Facility*

Picture 8 : *Emission Values (Half-Hour-Values)*



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Picture 7 : *Emission Values (Daily Mean Values)*

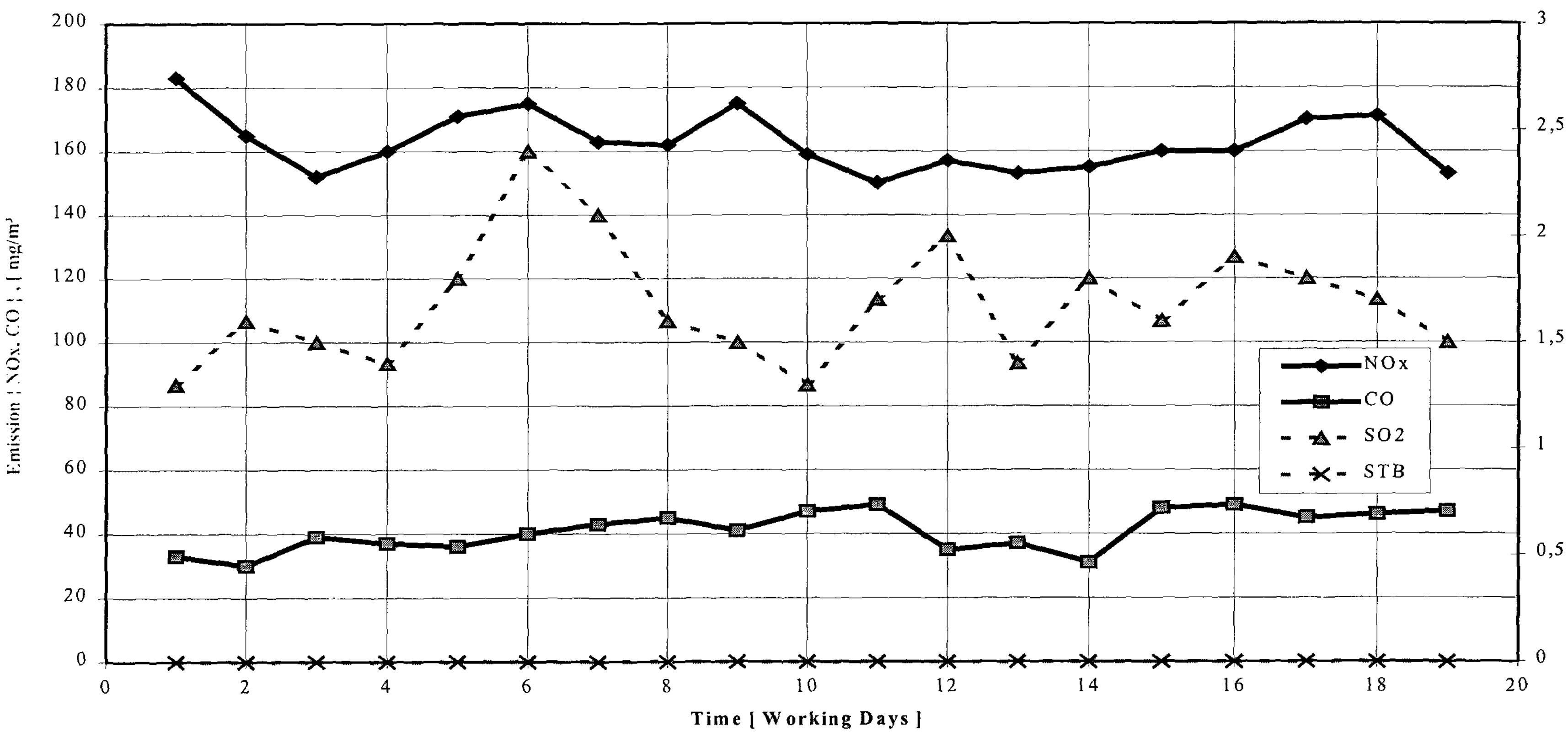

Figure 6: Disposal Facility (Waste Gas Purification) - Silberhütte